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(54) Title: A PHOTOCATALYST CONTAINING TITANIUM OXIDE, THE PRODUCTION METHOD AND USE OF THE SAME

(57) Abstract: The invention relates to a photocatalyst containing titanium dioxide, to a method for using it and to its application. A sulphurous titanium dioxide hydrate precipitate is precipitated from an acid titanium oxysulphate solution at a temperature below the boiling point of the solution, e.g. in the range from 70 to 100°C, using crystal nuclei and without addition of base. The precipitate is separated, washed and calcinated. The photocatalytic titanium dioxide thus obtained has a specific area in the range from 100 to 250 m<sup>2</sup>/g and a 0.3 to 5% sulphur concentration. Catalytic activity has been confirmed in asetal dehyde decomposition and in anionic (SNC)<sub>2</sub> radical formation.

**WO 03/082743 A1**

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**A photocatalyst containing titanium oxide, the production method and use of the same**

- 5 The invention relates to a method for preparing a photocatalyst containing titanium dioxide, the photocatalyst prepared by this method and the use of the photocatalyst thus obtained.

10 Titanium dioxide, of which the major production portion is used as a pigment, is prepared by the "sulphate method", in which an ilmenite concentrate is reacted with sulphuric acid at high temperature, and iron is separated from the obtained solution by precipitating in the form of ferrosulphate. The remaining acid titanium oxide sulphate solution is concentrated and heated to its boiling temperature, at which  
15 titanium is precipitated in the form of metatitanic acid. The precipitate is separated and transformed into titanium dioxide by calcination at a temperature of about 900°C.

In an optional method for preparing titanium dioxide, titanium brine is neutralised at ambient temperature by addition of alkaline or ammonium hydroxide, and then  
20 titanium precipitates as orthotitanic acid. DE patent specification 3 439 217 describes partial neutralisation, in which a minor portion of the concentrated titanium sulphate solution is first combined with alkali at 85 to 90 °C, and this partial solution is subsequently added to a titanium sulphate solution at a temperature of 85 °C, which is then heated to the boiling point, at which titanium is  
25 precipitated.

Precipitation under various conditions of titanium dioxide hydrates included in pigment production has been studied in Jalava et al., Ind. Eng. Chem., Res. 2000, 39, pages 349 to 361. In addition to precipitation in the sulphate method and base  
30 precipitation from a titanium chloride solution, the authors examine precipitation at temperatures of 70 °C and 90 °C, with an aqueous solution prepared from titanyl sulphate as the material. The result was either metatitanic acid or orthotitanic acid, which were produced in the solution as the primary particles originally present in the solution adhered to each other, forming aggregates, which then joined into  
35 larger particles. The temperature increase and the low concentration of the solution were observed to foster orthotitanic acid production. However, precipitation was

slow and yields low due to the fact that titanium in ionic form precipitated only with a delay.

Besides the use as a pigment, the aptitude of titanium dioxide as a photocatalyst has also been widely studied. The development of a photocatalyst acting in the area of visible light has been an objective for chemists for many years. They have aimed at a  $\text{TiO}_2$  catalyst operating with solar energy, which would oxidise water or air pollutions. Usually titanium dioxide in anatase form absorbs solar radiation at wavelengths under 390 nm, whereby the electron excitation contributes to the formation of oxygen or hydroxy radicals. Radicals, in turn decompose aldehydes,  $\text{NO}_x$  gases and organic solvents. The advantages of titanium dioxide when used as a catalyst include chemical inertia and atoxity, yet involving the drawback that with both the crystal forms of titanium dioxide, anatase and rutile, the energy difference between various electron excitation states (band gap) is approx. 3 eV, the corresponding photon being in the UV area beyond visible light. This is why there have been attempts to transform titanium dioxide so as to make it operate also in the area of visible light at wavelengths above 400 nm.

So far, titanium dioxide intended as a photocatalyst has mostly been produced from titanium tetrachloride either in the gaseous phase or from a solution by precipitation with a base. Precipitation as orthotitanic acid produces a large specific area in the final calcinated titanium dioxide, this area being favourable in terms of catalytic activity. Modification of the catalyst so as to make it functional in the area of visible light has been attempted by using various additives. Thus, for instance, catalysts have been doped with various metals, such as iron, chromium or cobalt, which have been impregnated in titanium dioxide hydrate precipitate before calcination of this. Asahi et al., SCIENCE 293 (2001), pages 269 to 271, have doped  $\text{TiO}_2$  with nitrogen using sputtering technique and tested the resulting product by decomposing gaseous acetal dehyde. In EP patent specification 1138 634 A1, photocatalytic activity of visible light has been sought with the use of ammonia gas. In this patent specification, calcination of titanium hydroxide in air without ammonia treatment yields poor activity in visible light. Muggli et al., Applied Catalysis B: Environmental 32, 2001, pages 181-194, managed to increase the specific area of titanium dioxide photocatalysts and their activity in specific conditions by adding sulphate ions before calcination.

EP patent specification 1 174 392 describes the production of photocatalytic titanium dioxide starting from a titanium oxysulphate solution, which has first been evaporated as solid titanium oxysulphate. This has subsequently been reacted with ammonia, eventually followed by calcination. A gas that was supposed to be  
5 nitrogen and sulphuric dioxide separated from the obtained titanium dioxide at high temperature.

Other known ways of regulating the specific area and other properties of titanium dioxide photocatalysts comprise regulation of the precipitation and calcination  
10 temperatures and other production conditions of titanium hydrate. There have also been attempts to increase the photoactivity of titanium dioxide by reducing part of the titanium to trivalent titanium. However, this involves the problem of the instability of trivalent titanium, its tendency to reoxidise to tetravalent titanium.

15 The purpose of the present invention is to provide a new method for preparing titanium dioxide photocatalysts, which eliminates the prior art problems mentioned above while producing a catalyst having increased activity in the area of visible light. The production of titanium dioxide in accordance with the invention is characterised in that from an acid solution containing titanium oxysulphate at a  
20 temperature under the boiling point of the solution is precipitated by addition of crystal nuclei a sulphurous titanium dioxide hydrate precipitate, said precipitate being separated and subsequently subjected to thermal treatment in order to obtain a crystalline sulphurous product.

25 A suitable reactant of the method of the invention comprises acid titanium oxysulphate solution obtained from sulphuric acid dissolution of ilmenite, at least the major portion of iron having been removed from the solution. The invention can thus be simply carried out by following an industrial sulphate process known *per se*, excepting that the precipitation temperature is lower than the one used in the  
30 sulphate process, below the boiling point of the solution. The precipitation step of the method has very high yield and separation of the precipitate from the liquid phase is easy. Calcination can be performed in air at a relatively low temperature without the ammonia treatment required in prior art. The calcinated end product is stable, and it has been stated to have an excellent photocatalytic effect at visible  
35 light wavelengths in different reactions. Higher activity in acetaldehyde decomposition and formation of  $(\text{SCN})_2$  anion radical than previous titanium

dioxide photocatalysts have been determined for the product, the reactions having been used in the preliminary testing of the invention.

5 The sulphur obtained in the product in accordance with the invention is based on precipitation from the sulphate solution conducted in acid conditions. Besides the presence of sulphur, the observed high catalytic activity may relate to the precipitation of titanium as orthotitanic acid. The precipitate has been confirmed to dissolve into 43% sulphuric acid at a temperature of 60 °C forming a 22% TiO<sub>2</sub> solution. Orthotitanic acid produces a large specific area in the product, which is  
10 favourable in terms of photocatalytic activity. However, we stress that these assumptions are not by any means intended as a restriction of the invention.

As precipitation is activated in the method of the invention by means of crystal nuclei added as seed to the solution, it is not necessary to change the pH of the  
15 solution in the precipitation phase. In other words, the method operates without base addition, which is a substantial difference from previous methods of precipitating titanium dioxide.

The advantageous precipitation temperature range in accordance with the invention  
20 is 70 to 100 °C. Tests showed that the most active catalyst had precipitated at a temperature of 80 °C. When the precipitation temperature increases above this, results indicate that the catalytic activity starts decreasing.

The crystal nuclei used as precipitation seed, which may have a size of a few  
25 nanometres, are most preferably anatase. With anatase seeding the final calcinated titanium dioxide is also in anatase form, which is a more active catalyst than rutile.

Calcination of the hydrate precipitate is conducted in the temperature range 100 to 500 °C, most preferably in the temperature range 200 to 500 °C. The catalytic  
30 activity has been observed to decrease above and under this calcinations temperature range.

The activity of the titanium dioxide photocatalyst prepared in accordance with the invention may be enhanced under the action of iron or chromium present in the  
35 catalyst. If the precipitating solution containing titanium oxide sulphate is prepared by the sulphate method, ferric iron can be left in the solution so as to precipitate as hydroxide along with titanium. Chromium may be added as a doping agent to the

precipitate, and the amount of iron can also be increased by means of doping. Results show that trivalent chromium and iron have an enhancing action on catalysis especially at visible light wavelengths above 420 nm and particularly when they are simultaneously present in the catalyst.

5

The photocatalyst containing titanium dioxide of the invention is characterised by the crystalline particulate product having a specific area of 100 to 250 m<sup>2</sup>/g and of the product containing 0.3 to 5% of sulphur, preferably 0.5 to 4%, and most preferably 1 to 4%. The titanium dioxide is most preferably in anatase form, and  
10 besides sulphur, the product may contain chromium, advantageously 0.05 to 2% and most preferably 0.1 to 1%, and iron, preferably 0.05 to 3% and most preferably 0.1 to 1.5%. The photocatalyst of the invention can be prepared as in the description of the method given above.

15 The use of the titanium dioxide of the invention described above or prepared by the method explained above comprises generally decomposition of organic compounds or microorganisms at wavelengths in the visible light area of photocatalysation. In accordance with the invention, the catalyst may be used mixed in the binder in a honeycomb catalytic structure and in coating compositions for various purposes,  
20 such as self-purifying surfaces, car paints, glass, lamp and shade surfaces and anti-fogging coatings.

The invention is explained in greater detail below by means of embodiment examples illustrating the preparation of a photocatalyst and by the results obtained  
25 with these catalysts.

### Example 1

30 An ilmenite concentrate and sulphuric acid were allowed to react mutually at high temperature. After this, the metal sulphates formed were dissolved in diluted sulphuric acid. The insoluble residue was filtered separately. The ferric iron of the solution was reduced into ferrous form and part of the iron was removed by crystallisation in the form of ferrosulphate by cooling the solution.

35 Measured at 60 °C, the main components of the solution thus formed were 18% of sulphuric acid, 9.5% of titanium dioxide and 3.6% of iron (Fe<sup>2+</sup>). 9800 g of this solution was placed in a precipitation flask into a water bath at a temperature of 70

°C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was further separated by precipitation for 20.5 hours. The precipitation yield was then 93.8%.

- 5 The precipitate was filtered and washed with water (2 dm<sup>2</sup> of water/350 g TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 4 hours.

The sample had a specific area of 187 m<sup>2</sup>/g.

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### Example 2

The procedure was the same as in example 1, but the titanium hydrate precipitate was calcinated at a temperature of 400 °C for 4 hours.

15

### Example 3

The procedure was the same as in example 1, but the titanium hydrate precipitate was calcinated at a temperature of 500 °C for 4 hours.

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### Example 4

The procedure was the same as in example 1, but the titanium hydrate precipitate was calcinated at a temperature of 600 °C for 4 hours.

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### Example 5

The procedure was the same as in example 1, but the titanium hydrate precipitate was calcinated at a temperature of 200 °C for 4 hours.

30

### Example 6

- 35 9800 g of the solution used in example 1 was placed in a precipitation flask into a water bath at a temperature of 80 °C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was separated by precipitation for 5 hours. The precipitation yield was then 93.2%.

The precipitate was washed with water (2 dm<sup>3</sup> of water / 350 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 4 hours.

#### 5 Example 7

The mass that had been precipitated, filtered and washed in example 1 was dissolved in concentrated sulphuric acid, and water was added to the solution to a sulphuric acid concentration of 31.7% measured at 60 °C and a titanium dioxide concentration of 239 g/dm<sup>3</sup>. 1225 g of this solution was placed in a precipitation flask in a water bath at a temperature of 70 °C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was separated by precipitation for 20 hours. The precipitation yield was then 96.7%.

15 The precipitate was washed with water (2 dm<sup>3</sup> of water / 350 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 4 hours.

#### 20 Example 8

7022 g of the solution used in example 1 was placed in a precipitation flask in a water bath at a temperature of 90 °C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was separated by precipitation for 3 hours. The precipitation yield was then 93.1%.

25 The precipitate was washed with water (6 dm<sup>3</sup> of water / 350 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 4 hours.

#### 30 Example 9

7015 g of the solution used in example 1 was placed in a precipitation flask into a water bath at a temperature of 100 °C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was separated by precipitation for 2 hours. The precipitation yield was then 94.5%.

The precipitate was washed with water (6 dm<sup>3</sup> of water / 350 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 4 hours.

### Example 10

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An ilmenite concentrate and sulphuric acid were allowed to react at high temperature. After this, the metal sulphates formed were dissolved in diluted sulphuric acid. The insoluble residue was filtrated separately. Part of the ferric iron of the solution was removed by crystallisation.

10

Measured at 60 °C, the main components of the solution thus formed were 21.3% of sulphuric acid, 8.6% of titanium dioxide and 2.5 of iron. 9495 g of this solution was placed in a precipitation flask in a water bath at a temperature of 70 °C, where it was stirred. To activate precipitation, 3% of nuclei in anatase form were added to the solution and the titanium hydrate precipitate was separated by precipitation for 20.5 hours. The precipitation yield was then 93.8%.

15

The precipitate was filtered and washed with water (2 dm<sup>2</sup> of water/212 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at a temperature of 300 °C for 2 hours.

20

### Example 11

100 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 10 was mixed with 1.25 ml of a CrCl<sub>3</sub> solution having a concentration of 115 g/l.

25

The mixture was calcinated at 300 °C for 2 hours.

### Example 12

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100 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 10 was mixed with 5 ml of a VCl<sub>3</sub> solution having a concentration of 118 g/l.

35

The mixture was calcinated at 300 °C for 2 hours.

**Example 13**

100 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 10 was mixed with 0.25 ml of an  $\text{NbCl}_5$  solution having a concentration of 40 g/l.

The mixture was calcinated at 300 °C for 2 hours.

**Example 14**

100 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 1 was mixed with 5 ml of a  $\text{CrCl}_3$  solution having a concentration of 115 g/l. When the chromium and iron concentrations were analysed, part of the iron contained in the solution was observed to be oxidised and mixed with this precipitation mass. A 1.0% Cr concentration and a 0.1% Fe concentration were analysed.

The mixture was calcinated at 300 °C for 2 hours.

**Example 15**

100 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 1 was mixed with 11.3 ml of a  $\text{Cr}(\text{SO}_4)_3$  solution having a concentration of 10.4 g/l. Ferrosulphate was additionally added so as to get a Cr concentration of 0.16% and a Fe concentration of 1.5%.

The mixture was calcinated at a temperature of 300 °C for 2 hours.

**Example 16**

100 g of the titanium dioxide hydrate mass obtained by filtering and washing in abundant water as in example 6 was mixed with 2.2 ml of a  $\text{CrCl}_3$  solution having a concentration of 115 g/l. the titanium dioxide had a Cr concentration of 0.48%.

The mixture was calcinated at 300 °C for 1.5 hours.

**Example 17**

Ammonia was added to 200 g of the titanium dioxide hydrate mass obtained by filtering and washing with abundant water as in example 6 at ambient temperature for pH regulation to 6.5. After neutralisation, the precipitate was carefully washed with water in order to remove ammonia sulphate. Then 30 g of titanium oxide hydrate mass neutralised to pH 6.5 was mixed with 3.7 ml of a  $\text{Cr}_2(\text{SO}_4)_3$  solution (8.0 g of Cr/l). 0.22 ml of ferrisulphate solution was added to this (148 g of Fe/l) and the mixture was calcinated at a temperature of 200 °C for 2 hours.

**Example 18**

90 g of the titanium dioxide hydrate mass obtained by filtering and washing as in example 8 was mixed with 7.8 ml of a  $\text{Cr}_2(\text{SO}_4)_3$  solution having a concentration of 8.4 g/l. 4.6 ml of a ferrisulphate solution (15.5 g of Fe/l) was added and the mixture was calcinated at 100 °C for 6 hours.

**Example 19 (comparative)**

The concentrated solution used in example 7 was diluted with water so as to get a sulphuric acid concentration of 20.1% and a titanium dioxide concentration of 129 g/l. 100 ml of this titanium sulphate solution was added to 100 ml of a 20% ammonia solution from a dropping funnel at low temperature, whereby titanium hydrate precipitated. At the end of the addition, the pH was 8.7. The mixture was boiled for 1 hour at 70 °C.

The precipitate was washed with water and calcinated at a temperature of 300 °C for 2 hours.

**Example 20 (comparative)**

The reactant was a titanium dioxide chloride solution ( $\text{TiOCl}_2$ ), which was diluted with water to a content of 40 g/dm<sup>3</sup> of  $\text{TiO}_2$  and 80 g/dm<sup>3</sup> of HCl. 0.594 dm<sup>3</sup> of this solution was placed in a precipitation flask into a water bath at a temperature of 70 °C, where it was stirred and titanium hydrate precipitated.

The precipitate was washed with water (2 dm<sup>3</sup> of water/350 g of TiO<sub>2</sub>). The titanium hydrate precipitate was calcinated at 300 °C for 3 hours.

#### Example 21 (comparative)

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The comparative substance comprised a commercial product of anatase type FINNTi S140. The sample had a specific area of about 250 m<sup>2</sup>/g.

#### Example 22 (comparative)

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The comparative substance comprised a commercial product of anatase type (approx. 30% of rutile) Degussa 25. The sample had a specific area of about 50 m<sup>2</sup>/g.

#### 15 Example 23

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A photocatalytic dispersion was prepared by mixing 240 g of the product of example 1, 180 g of water, 18 g of the product Disperbyk 190 (Byk-Chemie) and 6 g of the product Foamaster VL (Henkel-Nopco). Water, Byk 190 and Foamaster were first weighed into a beaker. Then the product of example 1 was added gradually during the dissolver mixing (5 minutes). Finally the mixture was dispersed in a bead mill for 20 min.

#### Photoactivity measurements

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##### 1. Asetal dehyde oxidation

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The photoactivity of titanium oxides of examples 1 to 18 in the visible light area was determined using the titanium oxides as photocatalysts in asetal dehyde oxidation in a 0.5 litre reactor. In two measurement sets the light source was a 150 W xenon lamp, whose UV light was filtered off with 400 nm and 420 nm light filters. The asetal dehyde concentration was determined by gas chromatography comprising a FID detector (Hewlett Packard 5890). The rate of asetal dehyde decomposition in the system was calculated for 2 hours: decrease in the peak area/120 min. The angular coefficient was determined by means of linear regression. The results are shown in the following table.

Table

	Sulphur concentr./%	Fe concentr. ppm	Cr concentr. ppm	Specific area m <sup>2</sup> /g	Photoactivity Filter 400 nm Area/min	Photoactivity filter 420 nm Area/min
Example 1	2.6	34	10	187	1530	540
Example 2	2.5	34	10	126	1800	440
Example 3	2.4	34	10	95	1340	410
Example 4	1.3	34	10	54	244	
Example 5	3.0	34	10	244	1540	280
Example 6	3.2	27	17	165	2500	600
Example 7	2.9	16	2	212	1470	380
Example 8	1.7	20	18	166	2460	406
Example 9	1.8	18	16	179	940	
Example 10	3.9	5100	4	103	1360	814
Example 11	4.2	5100	4500	172	1800	1600
Example 12	3.9	5100	4	215	200	
Example 13	3.9	5100	4	223	400	
Example 14	3.9	1000	10000	172	1840	1470
Example 15	3.8	15000	1600	170	2700	2430

Example 16	3.3	9	4800	201	1470	1340
Example 17	0.5	2300	1700	202	1840	
Example 18	2.7	1160	1900	259	3300	
Example 19	0			116	0	0
Example 20	0			38	290	
Example 21	<0.3			250	60	
Example 22	0			50	295	70

The photoactivity of the product in example 15 was also measured using an ordinary fluorescent work lamp without light filter instead of a xenon lamp. The area/min. measured was 1060.

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## 2. $(\text{SNC}^-)_2$ anion radical formation

The photoactivity of the titanium dioxides obtained was tested by catalysing the formation of anionic  $(\text{SNC}^-)_2$  radical with the titanium dioxides in a potassium thiocyanate solution. 50 g/l of titanium dioxide was dispersed in a 1 M KSCN solution having pH 1. The formation and conservation of  $(\text{SNC}^-)_2$  radical was measured as a function of time.

With  $\text{TiO}_2$  prepared as in example 8,  $(\text{SNC}^-)_2$  radical formed at least up to 100 ps (formation life 158.9 ps) and a considerable amount still remained at 1 ns. The results showed that the transfer of the gap to SNC is considerably more efficient with the product of the invention than with other products, and hence they have higher photocatalytic activity.

The comparison comprised the products of examples 16 and 18, whose sulphur concentration and specific areas and also life values of the  $(\text{SNC}^-)_2$  radical obtained in femtosecond measurements differed from the values of the invention. With the

products of examples 16 and 18, the  $(\text{SNC})_2$  radical formed rapidly and subsequently began to disappear. At 1 ns, the radical was hardly observed.

### 3. Cleaning of aquarium water

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The inner filter of aquarium water was removed from an operating 40-litre aquarium, which had a distinct algal deposit on the walls and called for cleaning. The filter elements of the filter were rinsed with about 500 ml of water. A green solution containing algae was obtained.

10

A 50 ml sample of this solution was taken into a 70 ml beaker. The A solution was a comparative solution. 10 mg of  $\text{TiO}_2$  prepared as in example 1 was added into the B and C solutions and was stirred. Solutions A and B were stirred for 30 min. Solution C was exposed with an 8 W mercury discharge lamp having an intensity of about 1100 W/cm<sup>2</sup> and placed at a distance of 17 cm from the solution. The exposure period was 30 min.

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Clarification of the aquarium water was observed for solution C, but not for solutions A and B.

20

## Claims

1. A method for preparing a photocatalyst containing titanium dioxide, **characterised** in that from an acid solution containing titanium oxysulphate at a temperature under the boiling point of the solution is precipitated by addition of crystal nuclei a sulphurous titanium dioxide hydrate precipitate, said precipitate being separated and subsequently subjected to thermal treatment in order to obtain a crystalline sulphurous product.
2. A method as defined in claim 1, **characterised** in that the precipitation is conducted without addition of base.
3. A method as defined in claim 1 or 2, **characterised** in that the precipitation is conducted in a temperature range from 70 to 100 °C.
4. A method as defined in claim 3, **characterised** in that the crystal nuclei are anatase.
5. A method as defined in any of the preceding claims, **characterised** in that the precipitate separated from the solution is calcinated in air in the temperature range from 100 to 500 °C, preferably 200 to 500 °C.
6. A method as defined in any of the preceding claims, **characterised** in that the solution containing titanium oxysulphate is obtained by reacting ilmenite and sulphuric acid, by dissolving the sulphate thus formed and by removing at least part of the iron from the solution by reduction into ferrous form and crystallisation.
7. A method as defined in claim 6, **characterised** in that ferric iron is left in the solution, so that the titanium dioxide hydrate precipitate obtained contains iron.
8. A method as defined in any of the preceding claims, **characterised** in that a chromium(III) compound is added to the precipitate before the thermal treatment.
9. A method as defined in any of the preceding claims, **characterised** in that an iron compound is added to the precipitate before the thermal treatment.

10. A photocatalyst containing titanium dioxide, **characterised** in that the crystalline particulate product has a specific surface area in the range from 100 to 250 m<sup>2</sup>/g and that the product contains 0.3 to 5%, preferably 0.5 to 4% and most preferably 1 to 4% of sulphur.

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11. A photocatalyst as defined in claim 10, **characterised** in that the major portion of titanium dioxide is in anatase form.

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12. A photocatalyst as defined in claim 10 or 11, **characterised** in that the product contains 0.05 to 2% of chromium, preferably 0.1 to 1%, and 0.05 to 0.3% of iron, preferably 0.1 to 1.5%.

13. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst operating at visible light wavelengths.

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14. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst in the decomposition of organic compounds or microorganisms.

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15. Use of the titanium dioxide prepared as in any of claims 1 to 9 as a photocatalyst in a coating composition.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00251

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01G 23/053, B01J 21/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, PAJ, EPO INTERNAL, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0675086 A2 (ISHIHARA SANGYO KAISHA, LTD), 4 October 1995 (04.10.95), page 3, line 27 - line 30; page 5, line 11 - line 14; page 5, line 55 - line 58, claim 3, examples 3 and 4	1-6,13-15
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X	Applied Catalysis A: General, Vol 2, 2001, Suzuko Yamazaki et al: "Effect of sulfate ions for sol-gel synthesis of titania photocatalyst", pages 97-102, see abstract, table 1 and fig 2	10-11
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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12 June 2003

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00251

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Y	EP 0924164 A2 (HOYA CORPORATION), 23 June 1999 (23.06.99), see paragraph [0005],[0006] and [0029]	7-9,12
A	Ullmann's encyclopedia of industrial chemistry, 5th edition, vol A20, 1992, ed.: Barbara Elvers et al, pages 276-278 -----	1-15

**INTERNATIONAL SEARCH REPORT**  
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